(19) JAPANESE PATENT OFFICE (JP)
(12) OFFICIAL GAZETTE FOR PATENT
PATENT APPLICATION (A)

(11) Japanese Official Patent Publication
Kokai S63-104878

43) Publication Date: May 10, 1988

(51) Int. Cl.[5] B41M 5/00
ID Code (s)
Intra-Bureau No: B-6906-2H

Number of Inventions: 2
Request for examination: not yet
(Total number of pages in the original: 13)

(54) Title of the Invention Recording Material and Its Inkjet Recording Method

(21) Patent Application No. 61-250032
(22) Filing Date: October 21, 1986

(72) Inventor: Naoya Morohoshi
Canon Inc.
3-30-2 Shimo Maruko, Otaku, Tokyo

(72) Inventor: Ryuichi Arai
Canon Inc.
3-30-2 Shimo Maruko, Otaku, Tokyo

(71) Applicant: Canon Inc.
3-30-2 Shimo Maruko, Otaku, Tokyo

(74) Representative: Patent Attorney Giichi Marushima

Specifications

1. Title of the invention
   Recording Material and Its Inkjet Recording Method

2. Claims
   (1) A recording material of an ink reception layer comprised of at least two layers containing particles that is a recording material where at least the particles of one of the ink reception layers of the recording material is comprised of spherical silica.

(2) A recording material as claimed in Claim 1 where the particles contained in each of the ink reception layers have differing average diameters.

(3) A recording material as claimed in Claim 2 where the average diameters of the particles contained in each layer are greater than 1μm.

(4) A recording material as claimed in Claim 1 where the outermost ink reception layer is the layer containing spherical silica.

(5) A recording material as claimed in Claim 1 where the average diameter of the secondary particles of the spherical silica is 0.5-35μm and the average diameter of the pores of the secondary particles is 30-400λ.

(6) A recording material as claimed in Claim 1 where the thickness of the outermost ink reception layer is 3-30μm.

(7) A recording material as claimed in Claim 1 where the thickness of the inner ink reception layer is 5-100μm.

(8) An inkjet recording method for a recording material that is an inkjet recording method for recording using a recording liquid containing a water-soluble dye as the recording agent where the recording material has at least two ink reception layers and at least one of which is comprised of spherical silica particles.

(9) An inkjet recording method as claimed in Claim 8 where the average diameter of the secondary particles of the spherical silica is 0.5-35μm and the average diameter of the pores of the secondary particles is 30-400λ.

(10) An inkjet recording method as claimed in Claim 8 where the surface tensile strength of the recording liquid at 25°C is 30-70dyne/cm.
(11) An inkjet recording method as claimed in Claim 8 where the moisture content of the recording liquid is 20-90wt%.

3. Detailed Description of this Invention

This invention relates to a recording material and its inkjet recording method, specifically a recording material and its inkjet recording method that imparts excellent high quality recorded images with properties such as excellent color development and ink dot shape.

(Existing Technology)

With inkjet recording, small droplets of various recording liquids (hereafter, ink) are generated and applied by a discharge method (such as an electrostatic absorption method, a method to cause mechanical vibration or displacement of ink using pressure elements or a method using the pressure of heating ink). These ink droplets are dispersed so that all or a portion adheres to a recording material such as paper for recording. There is interest in a recording method that conducts high-speed printing with many colors while generating a minimum of noise.

The ink used for inkjet recording is primarily water-based, for safety and suitability for printing. Standard paper has generally been utilized as the recording material. When using this type of paper for recording using liquid ink, it is generally necessary to avoid fading during application of the ink on the recording paper, and there is a desire for ink that can be rapidly dried after application without unexpected contamination of the surface of the paper.

With multi-color inkjet recording methods using at least two colors of ink, the following requirements must be satisfied.

1) even with quick absorption into the ink recording material, the subsequently applied ink combines with the initially applied ink so the ink dots are altered but do not run;
2) ink droplets that are dispersed on the recording material and the diameters of the ink dots do not get larger than desired;
3) ink dots that are nearly round, with smooth edges;
4) high density ink dots that do not fade at the edges;
5) a recording material with high whiteness that has a high level of contrast with ink dots;
6) ink colors that do not change regardless of the recording material;
7) less recording material changes (such as wrinkles, stretching) before and after recording;
8) sufficient resistance of the recorded image to oxidation and light in water and air;
9) less debris falling from the base and coating of the recording material.

To achieve these demands, several proposals have been presented in the past. For example, the official gazette for Kokai53-49113 to improve the wicking of ink dots proposed an inkjet recording paper containing water-soluble polymers in a wood pulp sheet. An example of a coated paper is the inkjet recording sheet with an ink absorption layer on a base layer as published in the official gazette for Kokai55-5830. The official gazette for Kokai55-1162 proposed an inkjet recording sheet constructed of at least two differing ink absorption layers. The technical theory in the official gazette for Kokai55-11829 reduces the wicking of the ink dots on the sheet while deep absorption of the ink into the sheet provides images with good quality in the same manner as any of the methods employing reflected or transmitted light. The inkjet recording material published in the official gazette for Kokai56-99693 provides water resistance via quaternary ammonium halide.

Also, a recording paper with synthetic amorphous silica as the inkjet recording material was

published (the official gazette for Kokai55-51583) and this recording material is an inkjet recording material that has advantages such as excellent color developmental properties for the recording agent but since the shape of the particles is not uniform and the dispersion of the particle diameter is wide, the dot shape is distorted so it is difficult to improve ink absorption without lowering the coating strength and causing debris to drop off.

As indicated above, it has been possible to improve the inkjet recording material but sufficient properties have not been obtained relative to high quality print demands.

(Problems this Invention is to solve)

The objective of this invention is to solve the problems that have not been resolved by current technology in the technical fields indicated above. In particular, with an inkjet recording method, there is a demand for color image recording using multiple ink colors. This proposes a recording material and its inkjet recording method that improves the color development properties, developed color density, ink absorption and dot shape.

(Means to Solve the Problems)

The following invention meets the aforementioned objectives.

The first structure of this invention is a recording material of an ink reception layer comprised of at least two layers containing particles that is a recording material where at least the particles of one of the ink reception layers of the recording material is comprised of spherical silica.

The second structure of this invention is an inkjet recording method for a recording material that is an inkjet recording method for recording using a recording liquid containing a water-soluble dye as the recording agent where the recording material has at least two ink reception layers and at least one of which is comprised of spherical silica particles.

(Operation)

Next is a detailed explanation of this invention. The main features of this invention conduct ink recording via a water-soluble recording agent as the recording material for the aforementioned layer construction. With these inks, the color development properties, developed color density, ink absorption and dot shape are all improved.

These inventors have conducted intensive research on the structural requirements of ink reception layers such as particles or adhesion for inkjet recording materials. They have succeeded at satisfying all of the properties listed above including color development properties, developed color density, ink absorption and dot shape with a recording material with a single ink reception layer.

For example, a recording material with a single ink reception layer has problems with reduced coating tensile strength, excessive ink dot diameters and reduced developed color density due to a reduction in the amount of binder added to enhance ink absorption.

On the other hand, when considering a recording device that corresponds to a high quality recorded image, it goes without saying that the recording material must provide sufficient ink absorption, appropriate ink dot diameters, excellent color development properties and high developed color density.

These inventors have made it possible to nearly independently control ink absorption and ink dot diameters by selecting the type of particle and particle diameter for each layer of a multiple ink reception layered recording material.

As the result of research conducted on developed color density, with the so-called reflected light method that exposes light from an image side to form an image on the recording material, the recording agent (dye) is at the very edge of the thickness of the ink reception layer surface and if the light dispersion on the ink reception layer is insufficient, the developed color density becomes even higher.

Based on this information, these inventors have succeeded at the objectives of this invention.

Next is an explanation of the recording material that is the main part of this invention.

The recording material in this invention succeeds in meeting the objectives of this invention with a sheet comprised of at least two ink reception layers containing particles, at least one of which contains spherical silica as the particles and ink comprised as indicated above.

A specific example of the recording material in this invention is shown in Figure 1. In this example, there is an ink reception layer formed of an outermost layer 1 (primary layer) and a secondary layer 2 on a base 3. There are particles 4 and particles 5 in each ink reception layer. The particle diameters of particles 4 are smaller than that of particles 5.

For the embodiment example for the recording material in this invention, the function of each ink reception layer in the recording material shown in Figure 1 is described as follows.

Ink from various coating methods contacts the surface of the ink reception layer and is absorbed. In this example, the particle diameters in the outermost layer are smaller than the particle diameters of the secondary layer so the spaces between particles in the outermost layer are smaller than those in the secondary layer and the ink absorption speed is slightly slower in the outermost layer. However, compared to a recording material with only a secondary layer, the ink wicking in the horizontal direction is greater so the ink dots are larger.

In this manner, it is possible to make the ink dots the optimal size by selecting the diameter of the particles in the outermost layer. Also, since the surface smoothness of the ink reception layer is improved, the coating tensile strength (pull resistance) is improved.

When using spherical silica particles in the outermost layer with average diameters in the range of 0.5-3.5μm and average pore diameter of the secondary particles in the range of 30-400λ, the light dispersion on the secondary particle surface and the light dispersion on the inside of the particles is reduced. There are more dye molecules in the outermost layer due to capillary condensation of the dye molecules around the surface of the secondary particles. As a result, in addition to improving the developed color density, the shape and size of the space between the secondary particles becomes more uniform so the dot shape is improved when compared to other amorphous particles.

The ink passing through the outermost layer is absorbed by the secondary ink reception layer but the diameters of the particles in this secondary layer are large so there are spaces for ink absorption, making it possible for large amount of ink to be absorbed quickly. For the particles in the secondary layer, porosity is desirable and since they are spherical, there is a large gap in the ink reception layer so synthetic spherical silica is recommended in particular.

In this example, the particle diameter of the particles in the outermost layer are smaller than the adjacent particles of the secondary layer but depending on the characteristics other than those desired, the particle diameter of the particles in the outermost layer can be larger than the particles of the secondary layer. Also,

depending on the situation, it is possible to add a third and fourth ink reception layer. The particles utilized in this invention should have average diameters in the range of 0.5μm-40μm and the difference in the average diameters of each layer should be at least 1μm, ideally at least 2μm.

The recording material in this invention can be obtained with a base of standard paper available in the marketplace, industrial paper, synthetic paper or plastic film, with the aforementioned ink reception layer on this base. If the base contains particles, it is possible to combine the ink reception layer with the base.

In addition to the spherical silica mentioned above, examples of the particles used in this invention include inorganic pigments such as talc, clay, kaolin, diatomaceous earth, calcium carbonate, calcium sulfate, barium sulfate, titanium oxide, zinc oxide, zinc carbonate, aluminum silicate, calcium silicate, magnesium silicate, aluminum hydroxide, aluminum oxide, synthetic amorphous silica and colloidal silica; organic pigments such as thermoplastic resins and thermosetting resins as well as resin powders or emulsions such as polyethylene, polymethacrylate, elastomers, ethylene-vinyl acetate polymers, styrene-acryl copolymers, polyester, polyacryl and polyvinyl ether, where at least one is recommended.

Synthetic spherical silica with surface area was used as the spherical silica in this invention.

The shape in this invention involved uniform particles so the ratio of minimum to maximum diameter was greater than 0.6, ideally greater than 0.8.

The spherical silica utilized in this invention was produced by forming spheres from silica gel as indicated below or with porous silica.

The silica gel is a three-dimensional combination of reactive orthosilicic acid $Si(OH)_4$ so mechanically it is considered a silicon dioxide polymer $SiO_2 nH_2O$.

The method used to prepare the orthosilicic acid involves silicone tetraoxide or sodium silicate. Alternatively, silica gel neutralizes the alkalinity of the water glass (main elements of Na_2SiO_3 and $Na_2Si_2O_3$) and after gelling, it can be produced by removing the water.

Regardless of the method, by altering the orthosilicic acid concentration, the pH of the reactant, the composition of the solvent or the agitation speed during the polymer reaction, it is possible to control the particle diameter and pore diameter of the silica gel. Spherical silica gel can be gelified by reduction of a polymer reactant on an oil layer or it can be produced using a method that gelifies by spraying into dry air.

With the aforementioned operation, only standard gels can be produced but by adding porous former such as dextran, a long chain fatty acid, soluble starch or MgO into a sodium silicate solution, gelification can occur. Next, porous silica can be produced by removing this by solvent extraction or water dispersion.

Another method for producing porous silica involves gelification of narrow silica gel by particle dispersion.

It is possible to produce porous silica with varying pore diameters using the aforementioned methods.

In this invention, to improve the retention of the inkjet recorded image, with any of the production methods above, all of the metals such as Al, Mg, Zn or Ca are contained in composite silicate and all types of inorganics and organics in organic metal compounds are acceptable for surface treatments utilizing spherical silica.

Spherical silica produced with the aforementioned methods have smooth shaped particles when compared to synthetic amorphous silica produced by pulverizing or dispersion and the particle diameter is very uniform. When spherical silica is used for inkjet recording paper, light distortion in the areas of ink adhesion is reduced and since the uniformity of the capillary diameter is improved, the recorded image developed color density and dot shape are both improved.

The secondary particles of spherical silica employed in this invention should have average diameters in the range of 0.5μm-35μm, ideally 2μm-30μm and optimally 2μm-15μm. If the average diameter is greater than this range, the image quality will be reduced and the ink dot shape will deteriorate, resulting in a distorted image.

Small particle diameters are recommended for the ink dot shape but if the particle diameter is smaller than 0.5μm, the distortion function will be greater between 0.2-0.4μm and the developed color density will be reduced, so it is not recommended.

There is an optimal range for the average pore diameter inside the spherical silica (the space between each particle) and the average pore diameter of the spherical silica for this invention should be in the range of 30λ-400λ. As the pore diameter increases, the pore capacity inside the secondary particles of the spherical silica increases so the ink absorption capacity also increases. However if the pore diameter is greater than 400λ, the capillary condensation of the dye molecules around the surface of the secondary particles becomes difficult so the developed color density deteriorates. If the pore diameter is less than 30λ, the ink absorption capacity will deteriorate so is not recommended.

The ink reception layer of the recording material in this invention is produced by application to a base where the main components include the aforementioned particles and a binder, followed by drying.

Binders utilized have the function of adhesion between particles and/or between particles

and the base or the ink reception layer so standard materials can be employed. At least one resin such as polyvinyl alcohol, acryl resin, styrene-acryl copolymer, ethylene-vinyl acetate copolymer, starch, polyvinyl butyral, gelatin, casein, ionomer, gum arabic, carboxy methyl cellulose, polyvinyl pyrrolidone, polyacryl amide, phenol, melanine, epoxy, and styrene-butadiene rubber can be used as desired. If using denatured polyvinyl alcohol containing silicon, the ink absorption and coating speed can be compatible and so is recommended in particular. The binder should be 3-150 parts per 100 parts of particles, ideally 10-100 parts will impart sufficient particle adhesion and the spaces on the ink reception layer must be small so the ratio is not particularly restricted.

Other elements in the coating liquid can be any type of additive such as dispersants, fluorescent dyes, pH control agents, defoamers, lubricants, preservatives, surfactants and water resisting agents.

Of these additives, the water resisting agent can be standard monomers, oligomers or polymers exhibiting dissociative cationic properties when dissolved in water. However, a polydiaryl amine derivative containing a quaternary ammonium base is recommended.

Coating solids should be approximately 1-50wt% and the coating can be applied using standard methods such as the roll coater method, the blade coater method or the air knife coater method. The coating should be applied on a base in the range of 1-50g/m^2 (dried coating weight). Ideally the coating would be in the range of 2-35g/m^2 (dried coating weight).

The thickness of each ink reception layer of the recording material in this invention should be determined according to the characteristics required of the recording material, specifically ink absorption, ink dot diameter and developed color density. However, the outermost layer should be in the range of 3-30μm while the ink reception layer under the secondary layer should be 5-100μm.

This invention can involve a recording material with only an ink reception layer on the base and can exhibit surface smoothness by super calendaring.

Next, the ink used in the recording method in this invention should exhibit surface tensile strength at a temperature of 25°C that is in the range of 30-70 dyne/cm, recommended in the range of 40-65 dyne/cm and ideal in the range of 40-60 dyne/cm with a recording material containing water-soluble dyes and other additives. If the ink used has a surface tensile strength that is lower than this range during printing, it will have good gloss relative to the recording material but the print dot wicking will be larger. On the other hand, if the ink used has a surface tensile strength that is greater during printing, the gloss will be poor relative to the recording material, resulting in ink absorption and dot density deterioration that is not recommended.

The water-soluble dyes that comprise the essential elements for the ink employed in the recording method for this invention should be water-soluble dyes such as direct dyes, acid dyes or food dyes.

Examples of the direct dyes include C.1 direct black 2,4,9,11,14,17,19,22,27,32,36,38,41,48,49,51,56,62,71,74,75,77,78,80,105,106,107,108,112,113,117,132,146,154,194;

C.1 direct yellow 1,2,4,8,11,12,24,26,27,28,33,34,39,41,42,44,48,50,51,58,72,85,86,87,88,98,100,110;

C.1 direct orange 6,8,10,26,29,39,41,49,51,102;

C.1 direct red 1,2,4,8,9,11,13,17,20,23,24,28,

31,33,37,39,44,46,47,48,51,59,62,63,73,75,77,80,81,83,84,85,90,94,99,101,108,110,145,189,197,220,224,225,226,227,230;
C.I direct violet 1,7,9,12,35,48,51,90,94;
C.1 direct blue
1,2,6,8,15,22,25,34,69,70,71,72,75,76,78,80,81,82,83,86,90,98,106,108,11,120,123,158,163,165,192,193,194,195,196,199,200,201,202,203,207,218,236,237,239,246,258;
C.1 direct green 1,6,8,28,33,37,63,64;
C.1 direct brown 1A,2,6,25,27,44,58,95,100,101,106,112,173,194,195,209,210,211;
For acid dyes: C.1 acid black
1,2,7,16,17,24,26,28,31,41,48,52,58,60,63,94,107,109,112,118,119,121,122,131,155,156;
C.1 acid yellow
1,3,4,7,11,12,13,14,17,18,19,23,25,29,34,36,38,40,41,42,44,49,53,55,59,61,71,72,76,78,99,111,114,116,122,135,161,172;
C.1 acid orange 7, 8, 10, 33, 56, 64;
C.1 acid red
1,4,6,8,13,14,15,18,19,21,26,27,30,32,34,35,37,40,42,51,52,54,57,80,82,83,85,87,88,89,92,94,97,106,108,110,119,129,131,133,134,135,154,155,172,176,180,184,186,187,243,249,254,256,260,289,317,318;
C.1 acid violet 7, 11, 15, 34, 41, 43, 49,75;
C.1 acid blue
1,7,9,22,23,25,27,29,40,41,42,43,45,49,51,53,55,56,59,62,78,80,81,90,92,93,102,104,111,113,117,120,124,126,145,167,171,175,183,229,234,236;
C.1 acid green 3, 9, 12, 16, 19, 20, 25, 27, 41;
C.1 acid brown 4, 14;
For food dyes:
C.1.food black 2;
C.1.food yellow 3, 4, and 5;
C.1.food red 2,3,7,9,14,52,87,92,94,102,104,105,106;
C.1.food violet 2;
C.1.food blue 1, 2;
C.1.food green 2, 3, but of course are not limited to these shown.

These water-soluble dyes are generally products used by dissolving in a solution made of water or water and an organic solvent. The elements should be utilized as a mixture of water and all types of water-soluble organic solvents but the moisture content in the ink should be controlled to a range between 20-90wt percent.

Examples of the aforementioned water-soluble organic solvents include alkyl alcohols with 1-4 carbon atoms such as methyl alcohol, ethyl alcohol, n-propyl

alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, tert-butyl alcohol and isobutyl alcohol; amides such as dimethyl formamide and dimethyl acetamide; ketones or ketone alcohols such as acetone and diacetone alcohol; ethers such as tetra hydrofuran and dioxane; polyalkylene glycols such as polyethylene glycol and polypropylene glycol; alkylene glycols where the alkylene group contains 2-6 carbon atoms such as ethylene glycol, propylene glycol, 1,2,6-hexane triol, thioglycol, hexylene glycol and diethylene glycol; lower alkyl ether groups of polyhydric alcohols such as ethylene glycol methyl (or ethyl) ether or triethylene glycol monomethyl (or ethyl) ether.

Of these many water-soluble organic solvents, polyhydric alcohols such as diethylene glycol or lower alkyl ether groups of polyhydric alcohols such as triethylene glycol monomethyl (or ethyl) ether are recommended. The polyhydric alcohols evaporate the moisture in the ink and have a tremendous effect as a lubricant to prevent nozzle blockage due to water-solubie dye deposits and so are particularly recommended.

Solubilizers can be added to the ink.

Representative solubilizers are cyclic ketones containing nitrogen and their targeted action is to rapidly improve solubility relative to the solvent of the water-soluble dye. Recommended for use are N-methyl-2-pyrrolidone and 1,3-dimethyl-2-imidazolidone.

Inks controlled by these types of elements impart excellent fixing properties to the recording material for recording properties (signal responsiveness, droplet stability, spray stability, long term continuous recordability and spray stability after long periods of not recording) and retention stability. It is possible to include each type of additive to enhance these properties. Examples include viscosity regulators including water-soluble resins such as polyvinyl alcohol and cellulose; any type of cationic, anionic or nonionic surfactants; surface tensile strength regulators such as diethanol amine and triethanol amine; pH regulators as buffers.

To mix ink used in an inkjet recording method where the ink carries a charge, add resistivity regulators such as lithium chloride, ammonium chloride and sodium chloride. It is possible to control thermal properties (such as specific heat, coefficient of thermal expansion, heat transfer coefficient) according to the action of thermal energy during inkjet recording by spraying ink.

For this invention, the recording method that involves recording by laying the aforementioned ink on recording paper effectively separates ink from the nozzle. A method of laying ink on the recording material by spraying is acceptable. Representative examples of this method include those noted in IEEE Transactions on Industry Applications, Vol IA-13, No. 1 (February and March 1977) and Nikkei Electronics, April 19, 1976, January 29, 1973 and May 6, 1974. These published methods are suitable for the method in this invention. Several of these are described. First comes the static electricity absorption method where there is a strong electrical field between the accelerator electrodes placed at the nozzle and several mm before it.

The ink particles from the nozzle are gradually extracted. The extracted ink moves between the deflecting electrodes and the information signal is applied to the deflecting electrodes for recording. The ink particles corresponding to the information signal without being deflected are sprayed. This method is effective for this invention.

The second method involves applying high pressure to the ink using a compact pump. The nozzles are vibrated mechanically via liquid crystal vibration elements and miniscule ink particles are forcibly sprayed. The ink particles sprayed are charged according to the information signal at the same time. The charged ink particles pass between the deflecting electrode plates and are deflected according to the amount of charge. There is an abbreviated version of this called the microdot inkjet method. With this method, the ink pressure and vibration conditions are set to specific values in a given range, and small or large ink droplets are generated from the tip of the nozzle. Only small diameters and small droplets are recorded in this method. The features of this method allow groups of tiny droplets to be generated from existing large diameter nozzles.

The third method is the piezo element method. In this method, the mechanism applying pressure to ink is not the mechanical mechanism such as a pump found in existing methods but utilizes piezo elements. An electrical signal is applied to a piezo element to cause mechanical displacement that applies pressure to the ink which is sprayed from the nozzles.

The method published in the official gazette for Kokai54-59936 employs thermal energy to generate severe volume changes in the ink. This causes the ink to be discharged from the nozzle as the inkjet method, which can be effectively utilized.

In this invention, there are thermoplastic resin particles in the outermost layer of the ink reception layer. After inkjet recording, the outermost layer is heated so it is transparent and a glossy image is created.

(Embodiment Examples)

Below is a detailed description of this invention using embodiment examples and comparative examples. The parts and % are unrestricted weight standards.

This invention is not limited to the embodiment examples given below.

Embodiment Examples 1-3, Comparative Example 1

Using standard high quality paper (brand name); average 81.4g/m^2, manufactured by Sanyo Kokusaku Pulp Inc.) as the base, coating liquids with the following compositions were applied on this base as a secondary ink reception layer to reach a dried coat weight of 20g/m^2, and as an outermost layer to reach a dried coat weight of 6g/m^2 using a bar coater. A standard process was used for drying, followed by lightly super calendaring to obtain the recording material for this invention and for Comparative Example 1.

Embodiment Example 1

(Secondary Layer)

Synthetic spherical silica (average diameter 18μm, average pore diameter 120λ)	100 parts
Denatured polyvinyl alcohol containing silicon (manufactured by Kuraray Co., Ltd, R-1130)	40 parts

Cationic resin 5 parts
(manufactured by Showa Polymers, Polyfix 601)
Water 660 parts

(Outermost Layer)
Synthetic spherical silica 100 parts
(average diameter 5μm, average pore diameter 80λ)
Denatured polyvinyl alcohol containing silicon 60 parts
(manufactured by Kuraray Co., Ltd, R-2105)
Cationic resin 5 parts
(manufactured by Showa Polymers, Polyfix 601)
Water 820 parts

Embodiment Example 2

(Secondary Layer)
Synthetic amorphous silica 100 parts
(manufactured by Fuji Dewison (transliteration), Siloid 620, average diameter 20μm)
Denatured polyvinyl alcohol containing silicon 40 parts
(manufactured by Kuraray Co., Ltd, R-1130)
Cationic resin 5 parts
(manufactured by Showa Polymers, Polyfix 601)
Water 660 parts

(Outermost Layer)
Synthetic spherical silica 100 parts
(average diameter 5μm, average pore diameter 80λ)
Denatured polyvinyl alcohol containing silicon 60 parts
(manufactured by Kuraray Co., Ltd, R-2105)
Cationic resin 5 parts
(manufactured by Showa Polymers, Polyfix 601)
Water 820 parts

Embodiment Example 3

(Secondary Layer)
Synthetic spherical silica 100 parts
(average diameter 18μm, average pore diameter 120λ)
Denatured polyvinyl alcohol containing silicon 40 parts
(manufactured by Kuraray Co., Ltd, R-1130)
Cationic resin 5 parts
(manufactured by Showa Polymers, Polyfix 601)
Water 660 parts

(Outermost Layer)
Synthetic amorphous silica 100 parts
(manufactured by Fuji Dewison (transliteration), Siloid 72, average diameter 4μm)
Denatured polyvinyl alcohol containing silicon 60 parts
(manufactured by Kuraray Co., Ltd, R-2105)
Cationic resin 5 parts
(manufactured by Showa Polymers, Polyfix 601)
Water 820 parts

Comparative Example 1

(Secondary Layer)
Synthetic amorphous silica 100 parts
(manufactured by Fuji Dewison (transliteration), Siloid 620, average diameter 20μm)
Denatured polyvinyl alcohol containing silicon 40 parts
(manufactured by Kuraray Co., Ltd, R-1130)
Cationic resin 5 parts
(manufactured by Showa Polymers, Polyfix 601)
Water 660 parts

(Outermost Layer)

Synthetic amorphous silica	100 parts
(manufactured by Fuji Dewison (transliteration), Siloid 72, average diameter 4µm)	
Denatured polyvinyl alcohol containing silicon	60 parts
(manufactured by Kuraray Co., Ltd, R-2105)	
Cationic resin	5 parts
(manufactured by Showa Polymers, Polyfix 601)	
Water	820 parts

Using the four types of inks listed below for the aforementioned recording material, bubbles were generated by an exothermic resistor and inkjet recording was conducted using a recording device containing on-demand inkjet recording heads (size 20x25µm, 128 nozzles, drive voltage of 24.5V, frequency 2KHz) that discharges ink using pressure. The inkjet recording suitability was then evaluated.

Yellow ink

C.1 direct yellow 86	2 parts
Diethylene glycol	30 parts
Water	70 parts

Magenta ink

C.1 acid red 35	3 parts
Diethylene glycol	30 parts
Water	70 parts

Cyan ink

C.1 direct blue 86	4 parts
Diethylene glycol	30 parts
Water	70 parts

Black ink

C.1 hood black	4 parts
Diethylene glycol	30 parts
Water	70 parts

(1) Dot Diameter

The diameters of 20 printed dots were measured using a microscope and the average value shown.

(2) Dot Shape
The actual dot shapes were observed using a microscope and nearly round shapes designated by O, slightly irregular shapes designated by Δ and irregular shapes designated by x.

(3) Color Development Properties
The clarity of the color of the inkjet recorded image was visually observed and comparatively ranked using O, O, Δ and x with excellent designated by O and poor designated by x.

(4) Developed Color Density
Using a Macbeth densitometer RD-918, the density of the cyan beta copy area was measured.

(5) Ink Absorption
After black beta copying, the ink volume absorbed in one second was indicated.
The higher the value, the greater the ink absorption.
These results are shown in Table 1.

Comparative Examples 2-4

Using standard high quality paper (brand name); average 81.4g/m^2) as the base, liquids with the following compositions were applied on this base using a bar coater to reach a dried coat weight of 26g/m^2. A standard process was used for drying, followed by lightly supercalendaring to obtain the recording material for Comparative Examples 2-4.

(Composition of Liquid for Application)

Particles	100 parts
Denatured polyvinyl alcohol containing silicon (manufactured by Kuraray Co., Ltd, R-1130)	40 parts
Cationic resin (manufactured by Showa Polymers, Polyfix 601)	5 parts
Water	660 parts

The particles used are shown as follows.

Comparative Example 2
Synthetic amorphous silica
(manufactured by Fuji Dewison (transliteration), Siloid 620)

Comparative Example 3
Talc
(manufactured by Fuji Talc Industries, LM-S1, average diameter 2.3μm)

Comparative Example 4

Methyl methacrylate resin

(product from Matsumoto Petroleum Products (Inc), Matsumoto Microsufair (transliteration) M-100, average diameter 10μm)

Inkjet recording was conducted on the recording materials from the aforementioned Comparative Examples 2-4 in the same manner as found in Embodiment Examples 1-3. An evaluation of the inkjet recording suitability was conducted and those results are shown in Table 1.

Embodiment Example 4

The following compositions of liquids were utilized for coating on the recording materials from Embodiment Example 1 using a bar coater to reach a dried coat weight of 3g/m^2. A standard process was used for drying and the recording material for Embodiment Example 4 of this invention was obtained. Inkjet recording was conducted on this recording materials in the same manner as found in Embodiment Examples 1-3. Next, it was heated for 2 minutes at 140°C and the outermost layer permeabilized for ink receptivity to obtain an image with gloss. This image was also evaluated in the same manner as previous examples. These results are shown in Table 1.

(Composition of Liquid for Application)

Low density polyethylene resin 0.1 part

(manufactured by Mitsui Petrochemical Industries (Inc), Chemibal M-200, average diameter 7μm, concentration 40%)

Ionomer resin 100 parts

(manufactured by Mitsui Petrochemical Industries (Inc), Chemibal SA-200, concentration 35%)

Surfactant 11 parts

(manufactured by Kanebo (Inc), Belex OT-P, concentration 70%)

Table 1

	Dot Diameter (μm)	Dot Shape	Color Development Properties	Developed Color Density	Inkjet Absorption (cc/cm^2)
Embodiment Example 1	112	O	O	1.66	3.83×10^{-3}
Embodiment Example 2	117	O	O	1.61	3.57×10^{-3}
Embodiment Example 3	114	O	O	1.55	3.71×10^{-3}
Embodiment Example 4	116	O	O	1.72	3.52×10^{-3}
Comparative Example 1	119	Δ	O	1.49	3.45×10^{-3}
Comparative Example 2	81	x	O	1.23	3.77×10^{-3}
Comparative Example 3	123	Δ	x	1.31	2.12×10^{-3}
Comparative Example 4	140	Δ	Δ	1.36	1.48×10^{-3}

(Effect)

The recording method in this invention utilizes a recording liquid containing a water soluble dye by recording on a recording material that has at least two ink-receptive layers, at least one of which is comprised of spherical silica and which have particles of differing average diameters.

The recording liquid is rapidly absorbed into the recording material and the dot shape has little distortion, excellent color development properties and a recorded image with excellent clarity of developed color density. When the surface tensile strength of the recording liquid is 30-70dyne/cm, it has the effect of simultaneously satisfying the color development properties, developed color density and dot shape.

The recording material in this invention contains spherical silica in the ink receptive layer and is suitable for inkjet recording that demands excellent image quality.

4. Brief Description of the Figures

Figure 1 is a cross-section figure showing the embodiment example of the recording material in this invention.

1....outermost layer

2....secondary layer

3....base
4....particles
5....particles

Patent Applicant: Cannon Inc
Representative: Giichi Marushima

(63-104878) (13)

Figure 1